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14. ABSTRACT We describe the synthesis and characterization, by single crystal X-ray analysis, of a 1D heteroditopic self-complementary tecton for halogen bonding. It was designed to also incorporate double bonds and to possess heteropolar π - π stacking groups in order to carefully control its supramolecular organization in the solid state. As a result of this supramolecular control, by UV irradiation in the solid state the compound dimerizes forming a 2D heterotetratopic self-complementary tecton tailored to halogen bonding based self-assembly. This 2D tecton crystallizes clathrating chloroform molecules.					
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Solid state synthesis under supramolecular control of a 2D heterotetratopic self-complementary tecton tailored to halogen bonding†‡

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We describe the synthesis and characterization, by single crystal X-ray analysis, of a 1D heteroditopic self-complementary tecton for halogen bonding. It was designed to also incorporate double bonds and to possess heteropolar π - π stacking groups in order to carefully control its supramolecular organization in the solid state. As a result of this supramolecular control, by UV irradiation in the solid state the compound dimerizes forming a 2D heterotetratopic self-complementary tecton tailored to halogen bonding based self-assembly. This 2D tecton crystallizes clathrating chloroform molecules.

Introduction

Solid state synthesis is one of the most fascinating and rapidly emerging fields of Chemistry.¹ The interest in this innovative solventless approach lies in the high yields, the reduced formation of undesired side-products, and sustainability thanks to the particularly low waste produced by these kinds of reactions. Moreover, the highly organized environment of the solid state is an attractive medium for conducting stereoselective reactions. In particular, the topochemical control of UV-promoted [2 + 2] cycloaddition reactions in the solid state represents a promising way to form covalent bonds in a regio- and stereoselective manner. The seminal work of Schmidt² clearly established the requirements two double bonds should meet for undergoing [2 + 2] photoaddition in the solid state. The olefins have to be oriented in a parallel manner and the distance between their centres has to be lower than 4.2 Å. This can be realized by achieving control over the pattern of organization of the unsaturated modules in their crystal packing.

However, the careful engineering of the supramolecular arrangement of the modules in the crystal packing is quite hard, owing to the sensitivity of crystal structure to molecular structure. It has been demonstrated that steering groups such as chloro, bromo, fluoro, trifluoro, and methoxy and acetoxy groups³ can force molecules to pack in the desired crystalline order. Also, the use of directing intermolecular interactions has proved fruitful in dictating the topochemical alignment of

olefins for photoreaction in the solid state and in solution.⁴ Among these interactions, π - π donor-acceptor interactions have been used extensively as a steering device for potentially photoreactive structures⁵ as these interactions present the advantage that π - π stacked aromatic rings lie at a distance that roughly corresponds to that needed for the photocyclization of double bonds in the solid state (typical cut-off distance of π - π stacking 3.9 Å).⁶

On the other hand, the use of non-covalent interactions to dictate the self-assembly of unsaturated molecules around templates provides a very reliable and efficient tool to force unsaturated modules to meet Schmidt's requirements. The regiocontrol in covalent bond formation has been recently achieved through the organization of olefinic modules by hydrogen bonding-based templates.⁷ Following an analogous strategy, we have used an N \cdots I halogen bonding (XB)⁸-based template to direct the topochemical alignment of double bonds in the solid state. Our template operated at two levels: intramolecular π - π interactions pre-organize the template arms, and the alignment of template arms is translated into the alignment of olefins at the distance needed for photoreaction, thanks to the highly directional N \cdots I XB. The [2 + 2] photocyclization of *trans*-1,2-bis(4-pyridyl)ethylene has given the corresponding cycloadduct stereospecifically.⁹

The formation of halogen-bonded supramolecular architectures has been extensively studied in our group.¹⁰ In most cases, telechelic donor (D) and acceptor (A) modules self-assemble by XB into infinite 1D chains in which D and A alternate systematically. On the other hand, only a few examples of heteroditopic self-complementary modules for XB (possessing XB-D and -A groups in the same molecular structure) have been described in the literature.¹¹ With this in mind, we have synthesized the 1D heteroditopic self-complementary tecton **4** tailored to XB-based self-assembly. It was designed in order to possess terminal XB-D and -A groups, and to incorporate electron-rich and electron-poor aromatics connected by a double bond. It was expected that such a molecule self-organizes into 1D infinite polar chains thanks to self-complementary XB. Moreover, as a result of heteropolar

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† The HTML version of this article has been enhanced with additional colour images.

‡ Electronic supplementary information (ESI) available: Figures of **4** and **5** and a DSC plot. See DOI: 10.1039/b605958a

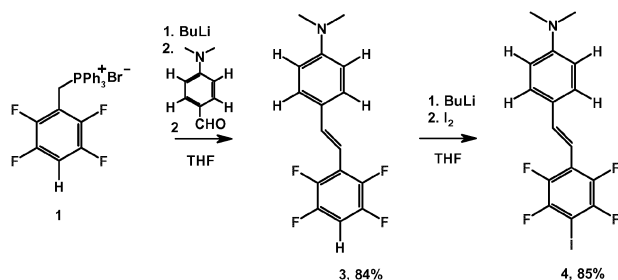
π - π stacking between adjacent chains, the double bonds of the different modules **4** should organize in order to meet Schmidt's requirements for regiocontrolled photocyclization in the solid state.

Results and discussion

The synthesis of the stilbene derivative **3** was achieved by a Wittig reaction between the phosphonium salt **1** and the *para*-(dimethylamino)benzaldehyde **2** in THF, by using *n*-BuLi. A 96 : 4 mixture of *trans* : *cis* isomers was obtained in 84% overall yield; stereoisomers were easily separated by chromatography. Iodination of the tetrafluorobenzene group¹² was carried out with *n*-BuLi-I₂ in THF affording **4** in 85% yield (Scheme 1).

Orange-yellow prismatic crystals have been obtained upon slow evaporation of the solvent at room temperature from a chloroform solution of the heteroditopic XB tecton **4**. The single crystal X-ray analysis of those crystals gave details on the molecular and supramolecular structure of **4**, which crystallizes in the monoclinic space group *P*2₁/*c*. The whole molecule assumes a nearly planar conformation to maximize the superposition of p orbitals as typical for all 4-dimethylaminostilbenes and polyfluorostilbenes. The two aromatic rings in **4** are slightly rotated relative to each other (by an angle of only 5.34°) and the N atom is characterized by a near planarity (C-N-C angles in the range 116.53–119.39°, Fig. 1). The coplanarity of tetrafluoroaromatic ring and double bond is strengthened by two intramolecular H···F hydrogen bonds (F1···H8 is 2.35 Å and F4···H7 is 2.43 Å).

As concerns the supramolecular organization of **4** in the crystal packing, the molecules are arranged in a head-to-tail fashion into 1D infinite chains, as expected for a telechelic self-complementary XB heteroditopic tecton. Two molecules approach each other in a perpendicular fashion (Fig. 2, the C_{Ar}-Nⁱ···I angle ($i = 1 + x, \frac{1}{2} - y, \frac{1}{2} + z$) is 97.38°). The Nⁱ···I distance is 3.093 Å, about 12% shorter than the sum of van der Waals radii for N and I (3.53 Å).¹³ The Nⁱ···I-C angle is 169.82°, in good agreement with an $n \rightarrow \sigma^*$ electron donation from N to I atoms. The head-to-tail arrangement of the dipolar modules **4** ensures that each 1D chain is polar. Coupling of antiparallel 1D dipoles¹⁴ and the π - π attraction between opposite quadrupolar moments (Fig. 2) generates a centrosymmetric 2D structure with adjacent chains running in opposite directions. These 2D structures are bonded together in the third dimension by only residual forces. There are two



Scheme 1 Synthesis of the 1D heteroditopic self-complementary tecton **4** tailored to XB.

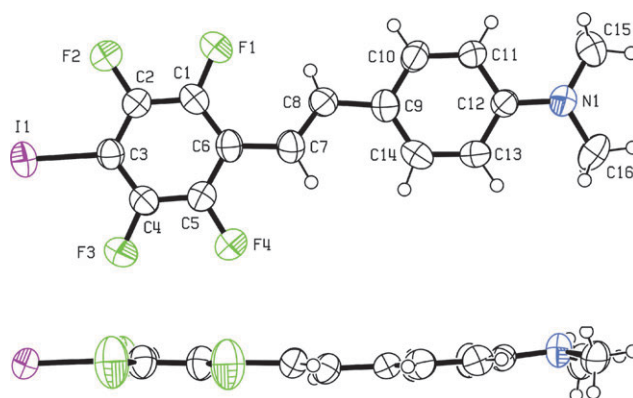


Fig. 1 Two ORTEP/III views of the structure of the self-complementary tecton **4** tailored to XB, with its numbering scheme. Ellipsoids at 50% probability level; H atoms not to scale. Colour code: black, carbon and hydrogen; blue, nitrogen; green, fluorine; purple, iodine.

types of interactions between aromatic rings: through the centre at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ only two antiparallel iodotetrafluoro benzenes interact, having 3.908 Å between their centroids (red full circles in Fig. 2), while through the centre at $\frac{1}{2}, 0, \frac{1}{2}$ two molecules are completely superposed with two pairs of tetrafluorobenzene and benzene ring centroids at a distance of 3.901 Å. Interestingly, the distance of the centroids of the double bonds for this couple of molecules is only 3.758 Å, nearly a pre-reactive state of the [2 + 2] reaction. Schmidt's rule is thus respected and the molecule undergoes solid state cycloaddition by UV photoirradiation.

The photoirradiation was performed by using a Rayonet instrument at 300 nm. Finely powdered crystals of tecton **4** were placed between two glass slides and irradiated for 24 h at room temperature to give the cycloadduct **5** in 80% yield, as a yellow powder (Scheme 2). The ¹H-NMR spectrum of the photoirradiated product revealed unequivocally the cyclobutane ring formation (single peak at 4.80 ppm, Fig. 3) and proved its complete regio- and stereospecificity.⁹

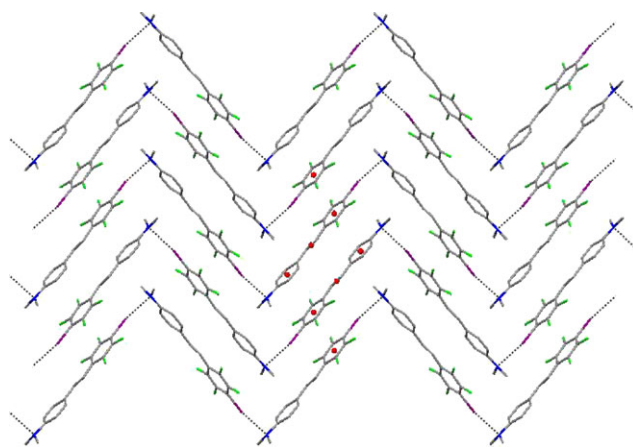
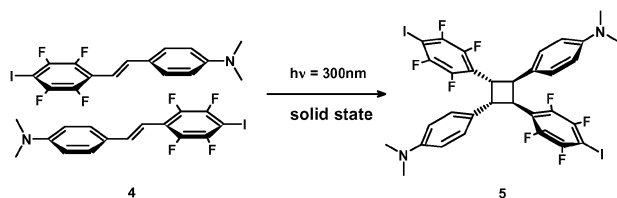


Fig. 2 A view down the crystallographic *c* axis of the crystal packing of the XB-based self-complementary tecton **4** (capped-stick style). Colour code: dark grey, carbon; blue, nitrogen; green, fluorine; purple, iodine. Halogen bonds are dotted black lines. Red full circles indicate the centroids of aromatic rings and double bonds.



Scheme 2 Solid state photoreaction of **4** to yield the 2D heterotetratopic self-complementary tecton **5** tailored to XB-based self-assembly.

As shown in Fig. 2, in the crystal packing the modules **4** are organized in well-defined and isolated photoreactive couples. A 100% maximum could be therefore predicted, but the photoradiation of **4** never leads to its total conversion into the corresponding cyclobutane derivative **5**. A detailed discussion of the reasons why the optimized yield is about 80% is far beyond the scope of this article. However, different irradiation times and wavelengths have never resulted in quantitative yields; moreover, an equilibrium mechanism responsible for the 80% yield has also been excluded. Cases of anomalous photoreactivity in the solid state have been already reported in the literature.^{3f,15} Low solid state yields could mean that the deformations in the reacting crystal prevent subsequent reac-

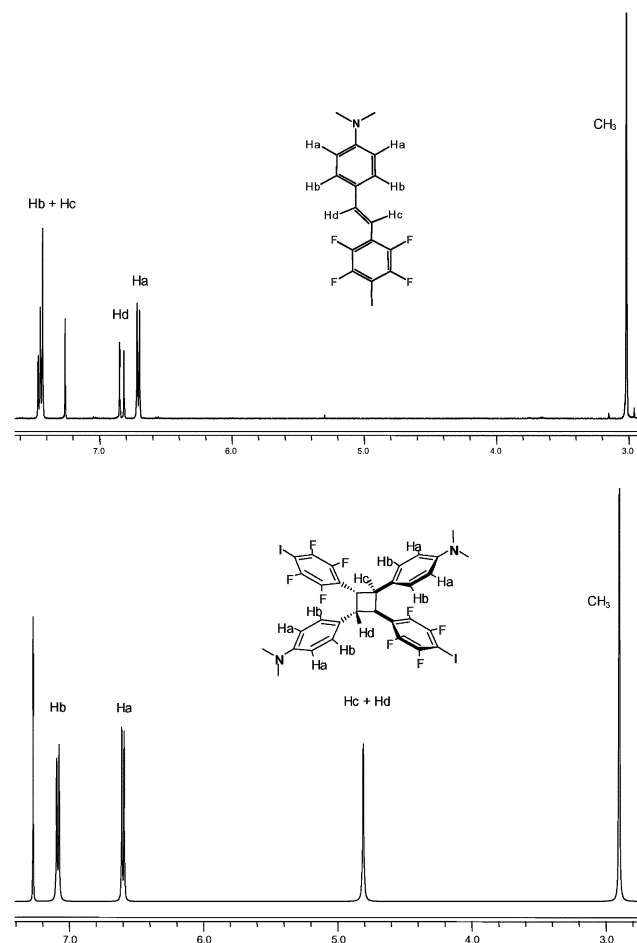


Fig. 3 ¹H-NMR spectra of XB-based self-complementary tectons **4** and **5**.

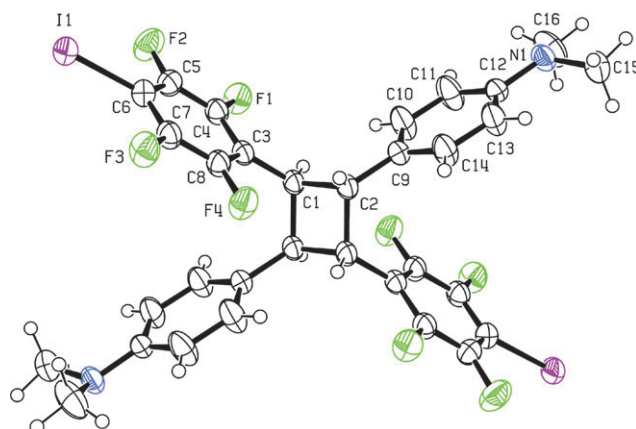


Fig. 4 A ORTEP view of structure of the XB-based self-complementary tecton **5** with its numbering scheme. Ellipsoids at 50% probability level; H atoms not to scale. Colour code: black, carbon and hydrogen; blue, nitrogen; green, fluorine; purple, iodine.

tivity. This can be ascribed to the high strength, directionality, and limited flexibility of XB, which is preserved in the photo-reacted crystal and probably induces a tremendous deformation of the crystal lattice of **4** on cyclobutane formation. In order to verify this hypothesis, we also studied the photoreactivity of **3**, which, missing the iodine atom, doesn't give XB. While this compound is isostructural with **4**, under irradiation it gives the corresponding cyclobutane with a 100% yield.¹⁶ This result can be a confirmation of the role played by XB in determining the anomalous photoreactivity observed in **4**.

Good-quality single crystals suitable for X-ray analysis of photoreacted product **5** were grown from chloroform. **5** Crystallizes in the monoclinic $P2_1/n$ space group as chloroform clathrate, with a 1 : 2, **5** : CHCl_3 ratio. Being consistent with the *E* stereochemistry of starting stilbene **4**, the cyclobutane derivative **5** has the *rctt* stereochemistry, with pairs of iodotetrafluorobenzene and dimethylanilino benzene pendants pointing to opposite directions with respect to the plane of the cyclobutane ring (Fig. 4). Cyclobutane **5** lies, in the crystal, on an inversion centre and being obtained through a solid state reaction between two molecules related by a centre of symmetry, it has a C_i stereochemistry. The conformation of **5** is influenced by two intramolecular $\text{H} \cdots \text{F}$ bonds, namely $\text{H1} \cdots \text{F1}$ (2.37 Å) and $\text{H2} \cdots \text{F4}$ (2.41 Å). These bonds lock the two fluorinated rings in a position nearly perpendicular to the cyclobutane ring (the dihedral angle between the mean square planes of the rings is 86.02°). The angle between the cyclobutane and the dimethylanilino rings is 57.78°.

The supramolecular organization of **5** in its crystal packing is governed by XB, which is by far the dominant intermolecular interaction. The cycloadduct **5** possesses two XB donor sites and two XB acceptor sites and behaves as a 2D heterotetratopic self-complementary tecton. In order to match its multivalency, a 2D infinite network is formed, which has a [4,4] topology, if the molecular centroids are used as nodes (Fig. 5). The $\text{N} \cdots \text{I}$ distance is 2.907 Å (17% shorter than the sum of van der Waals radii for N and I), while the $\text{N} \cdots \text{I}-\text{C}$ and $\text{C}-\text{N} \cdots \text{I}$ angles are 176.65° and 102.33°, respectively.

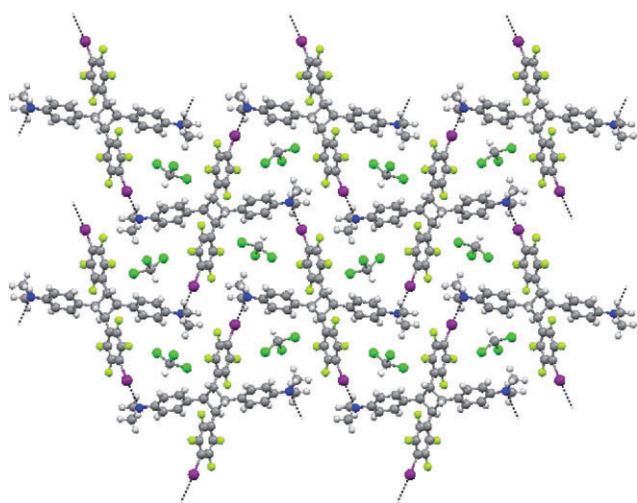


Fig. 5 A view down the crystallographic *c* axis of the crystal packing of the XB-based self-complementary tecton **5** (ball-and-stick style). Colour code: dark grey, carbon; light grey, hydrogen; blue, nitrogen; light green, fluorine; green, chlorine; purple, iodine. Halogen bonds are dotted black lines. Only one population of the two existing ones for the disordered chloroform molecules has been reported for the sake of clarity.

These values are consistent with a XB much stronger in tecton **5** than in **4**. This may be related to the higher electron density at N and a lower electron density at I in cyclobutane **5** than in stilbene **4**. Indeed, an intramolecular charge transfer, from the dimethylamino group to the tetrafluorobenzene ring, may occur in the stilbene **4** but it is prevented in the cyclobutane derivative **5**. As a consequence of this, the N atom in **5** is less planarized than in **4** (C–N–C angles in the range 113.40–117.28°).

The strength and directionality of the N...I XB prevent the tendency of tecton **5** to pack more efficiently by optimizing its pattern of self-complementary π – π stacking interactions. **5** Could form up to eight π – π interactions, which are expected to be particularly strong due to the opposite sign of the quadrupolar moments of the involved rings. On the contrary, no such interactions are formed and large columnar voids are present along the crystallographic *a* axis of the halogen-bonded [4.4] network of **5**. These voids are filled in with disordered chloroform molecules (see ESI, Fig. 6 and 7†), which orient their acidic hydrogen atoms towards the aniline rings (aniline ring-centroid–hydrogen distance 3.000 Å).¹⁷ Removal of the clathrated chloroform can be obtained by evaporation at reduced pressure, with the crystals retaining their shapes but becoming opaque. Differential scanning calorimetry (DSC) analysis of freshly prepared crystals of **5** has demonstrated that chloroform loss starts at room temperature and is complete at 130 °C. Melting of the sample occurs with decomposition at 251 °C (see ESI, Fig. 8†). While the overall crystal packing of **4** is determined by both N...I XB and π – π interactions, only N...I XB is present in **5**. Despite of the fact it is hard to directly correlate crystal packing and the strength of intermolecular interactions to melting points, nevertheless, the fact that the melting temperature of **5** is higher than the one of **4**, may be a further

indication that N...I XB in **5** is stronger than in **4**. This demonstrates the high coherence of the crystal matrix of **5**, which is based on multiple self-complementary XB.

Conclusions

Molecules with multiple binding sites are important tectons in supramolecular chemistry. Such heteromultitopic molecules are designed, *a priori*, to bind ion pairs¹⁹ and for the design of programmed metallosupramolecular architectures.²⁰ A fascinating goal is also the application of heteromultitopic molecules as “artificial enzymes” for directing the formation of covalent bonds.²¹ Heterotopic tectons for XB-based crystal engineering are definitely rare in the literature.¹¹ A particularly fine example of these tectons was reported by Desiraju *et al.* who synthesized the 4,4'-diiodo-4'',4'''-dinitrotetraphenylmethane and reported its single crystal X-ray structure. This heterotetraptopic self-complementary tecton based on XB self-assembles in a beautiful halogen-bonded diamondoid network. On the other hand, the covalent synthesis of this tecton is quite lengthy and gives a low overall yield.²²

With the aim of applying the tools of supramolecular chemistry to control the solid state synthesis of complex heterotopic tectons tailored to XB-based crystal engineering, we have synthesized the 1D self-complementary tecton **4**. On irradiation in the solid state, this tecton undergoes topochemically controlled photoreaction and yields the heterotetraptopic 2D self-complementary tecton **5**. This latter tecton self-organizes in the solid state thanks to strong and directional XB. A 2D architecture is formed wherein large voids are organized into columns along the crystallographic *a* axis. These voids are filled in with clathrated solvent molecules, which can be removed under low pressure.

The use of topochemically controlled photoreactions to conduct molecular synthesis by design of polydentate ligands for coordination-driven self-assembly of molecular frameworks has been proven to be a particularly effective strategy.^{5c,23} The results described in this paper show the first application of this strategy to the design of heteromultitopic tectons for XB-based crystal engineering.

Experimental

Materials and methods

Commercial HPLC-grade solvents were used without further purification. Starting materials were purchased from Sigma–Aldrich, Acros Organics, and Apollo Scientific. Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. ¹H-NMR and ¹⁹F-NMR spectra were recorded at ambient temperature with a Bruker AV 500 spectrometer. Unless otherwise stated, CDCl₃ was used as both solvent and internal standard in ¹H-NMR spectra. For ¹⁹F-NMR spectra, CDCl₃ was used as solvent and CFC₃ as an internal standard. IR spectra were obtained using a Nicolet Nexus FT-IR spectrometer equipped with an UATR unit. Chromatographic separations were performed on silica gel 230–400 mesh. The X-ray crystal structures were determined using a Bruker SMART APEX diffractometer. Melting points were

determined with a Reichert instrument by observing the melting and crystallizing process through an optical microscope. The photoreaction was carried out in a Rayonet RPR-100 instrument using monochromatic irradiation at $\lambda = 300$ nm. DSC analyses were carried out with a Linkam DSC600 hot stage ($10\text{ }^{\circ}\text{C min}^{-1}$).

Syntheses

***N,N*-Dimethyl-4-(*E*)-[2-(2,3,5,6-tetrafluorophenyl)-vinyl]aniline 3.** 250 mg (0.5 mmol) of phosphonium salt **1** were suspended in 1 mL of THF at $-70\text{ }^{\circ}\text{C}$. 0.7 mmol of *n*-BuLi (1.6 M) were added and the mixture was warmed up to room temperature. After 30 min, 150 mg (1 mmol) of aldehyde **2** were added and the mixture was left for 24 h while stirring. The solution was then washed with a saturated water solution of NH_4Cl , the aqueous phase was extracted 3 times with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4 . The crude material was purified by chromatography with *n*-hexane– CH_2Cl_2 mixture (2 : 1) as eluent to give 124 mg of product **3** (84% yield).

Yellow solid; $\lambda_{\text{max}} = 372$ nm; mp = $127\text{--}130\text{ }^{\circ}\text{C}$; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.45 (2H, d, $J = 8.8$ Hz, H arom.), 7.44 (1H, d, $J = 16.1$ Hz, CH), 6.87 (1H, d, $J = 16.1$ Hz, CH), 6.85 (1H, m, H arom.), 6.72 (2H, d, $J = 8.8$ Hz, H arom.), 3.02 (6H, s, CH_3); $^{19}\text{F-NMR}$ (470 MHz, CDCl_3): δ -144.7 (2F, m), -141.3 (2F, m); MS (ESI) m/z 295 (M^+). IR (powder, cm^{-1}): 3074, 2889, 2807, 1599, 1522, 1492, 1446, 1349, 1225, 1165, 1042, 969, 926, 850, 806, 705.

***N,N*-Dimethyl-4-(*E*)-[2-(2,3,5,6-tetrafluoro-4-iodophenyl)-vinyl]aniline 4.** 420 mg (1.42 mmol) of compound **3** were stirred in 4 mL of THF at $-70\text{ }^{\circ}\text{C}$. 1.71 mmol of *n*-BuLi (1.6 M) were added and the mixture was warmed up to room temperature. After 30 min, the reaction was cooled down to $-70\text{ }^{\circ}\text{C}$ and a solution of 505 mg (1.99 mmol) of I_2 in 1 mL of THF was added. After 2 h, the solution was then washed with a saturated water solution of $\text{Na}_2\text{S}_2\text{O}_3$, the aqueous phase was extracted 3 times with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4 . The crude material was purified by chromatography with *n*-hexane– CH_2Cl_2 mixture (2 : 1) as eluent to give 508 mg of product (85% yield).

Yellow solid; $\lambda_{\text{max}} = 382$ nm; mp = $210\text{ }^{\circ}\text{C}$; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.45 (1H, d, $J = 16.7$ Hz, CH), 7.44 (2H, d, $J = 8.8$ Hz, H arom.), 6.83 (1H, d, $J = 16.7$ Hz, CH), 6.71 (2H, d, $J = 8.8$ Hz, H arom.), 3.02 (6H, s, CH_3); $^{19}\text{F-NMR}$ (470 MHz, CDCl_3): δ -142.3 (2F, m), -123.3 (2F, m); MS (ESI) m/z 422 ($\text{M} + \text{H}^+$). IR (powder, cm^{-1}): 3089, 2899, 2820, 1595, 1519, 1466, 1445, 1332, 1219, 1192, 1165, 1125, 1054, 954, 940, 814, 797.

4,4'-[(1 α ,2 α ,3 β ,4 β)-2,4-bis-(2,3,5,6-tetrafluoro-4-iodophenyl)-cyclobutane-1,3-diyl]-bis-(*N,N*-dimethyl)aniline 5. Finely powdered crystals of **4** put between two glass slides were irradiated for 24 h. The crude material was then purified by chromatography with toluene as eluent to give the cycloadduct **5** in 80% isolated yield.

Pale yellow solid; mp = $251\text{ }^{\circ}\text{C}$ (dec.); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.07 (4H, d, $J = 8.6$ Hz, H arom.), 6.59 (4H, d, $J = 8.6$ Hz, H arom.), 4.80 (4H, s, CH), 2.89 (12H, s, CH_3);

$^{19}\text{F-NMR}$ (470 MHz, CDCl_3): δ -140.0 (2F, m), -122.5 (4F, m); MS (ESI) m/z 843 ($\text{M} + \text{H}^+$). IR (powder, cm^{-1}): 2994, 2882, 1595, 1517, 1465, 1008, 959, 914, 809, 750.

X-Ray crystallography

Crystal data. **4** $\text{C}_{16}\text{H}_{12}\text{F}_4\text{IN}$, $M = 421.17$, prism, $0.34 \times 0.27 \times 0.14\text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 10.174(2)$, $b = 11.671(2)$, $c = 13.043(4)\text{ \AA}$, $\beta = 103.26(3)^{\circ}$, $V = 1507.4(6)\text{ \AA}^3$, $Z = 4$, $D_c = 1.856\text{ g cm}^{-3}$, $F_{000} = 816$, MoK α radiation, $\lambda = 0.71073\text{ \AA}$, $\mu = 2.162\text{ mm}^{-1}$, $T = 293(2)\text{ K}$, $2\theta_{\text{max}} = 61.34^{\circ}$, 28 489 reflections collected, 4649 unique ($R_{\text{int}} = 0.0297$), 3733 with $I_o > 2\sigma(I_o)$, absorption corrections $T_{\text{min}}/T_{\text{max}} = 0.416$. Solved using *SIR2002*,²⁴ and refined with *SHELX-97*,²⁵ full-matrix least squares on F^2 , 217 parameters, 7 restraints on H atoms parameters, $GoF = 1.006$, $R_1 = 0.0423$, $wR_2 = 0.1048$ (all reflections), $-1.30 < \Delta\rho < 0.93\text{ e \AA}^{-3}$.

5 $\text{C}_{32}\text{H}_{24}\text{F}_8\text{I}_2\text{N}_2 \cdot 2\text{CHCl}_3$, $M = 1081.07$, prism, $0.40 \times 0.29 \times 0.17\text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 6.1825(8)$, $b = 18.9953(15)$, $c = 16.605(2)\text{ \AA}$, $\beta = 90.93(1)^{\circ}$, $V = 1949.8(4)\text{ \AA}^3$, $Z = 2$, $D_c = 1.841\text{ g cm}^{-3}$, $F_{000} = 1048$, MoK α radiation, $\lambda = 0.71073\text{ \AA}$, $\mu = 2.091\text{ mm}^{-1}$, $T = 293(2)\text{ K}$, $2\theta_{\text{max}} = 61.28^{\circ}$, 40 089 reflections collected, 5976 unique ($R_{\text{int}} = 0.0212$), 5206 with $I_o > 2\sigma(I_o)$, absorption corrections $T_{\text{min}}/T_{\text{max}} = 0.830$. Solved using *SIR2002*,²⁴ and refined with *SHELX-97*,²⁵ full-matrix least squares on F^2 , 279 parameters, 6 restraints on the aromatic H atoms parameters, $GoF = 1.045$, $R_1 = 0.0327$, $wR_2 = 0.0801$ (all reflections), $-0.47 < \Delta\rho < 0.67\text{ e \AA}^{-3}$. CCDC reference numbers 604218 (**4**) and 604217 (**5**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605958a

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